CHEMISTRY LETTERS, pp. 1917-1920, 1986.

Electrolytic N-Alkylation of Amines with Alcohols

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Electrolysis of the alcohol solution of amines in a one-chamber cell resulted in N-alkylation of the amines with sufficient current efficiencies. Platinum black particles suspended in the reaction mixture enhanced the efficiency due to their catalytic role for hydrogenation of a Schiff base intermediate.

Alcohols are good N-alkylation agents among many reported processes of amine N-alkylation. Although several transition metals and their complexes sufficiently catalyze the N-alkylation with alcohols,[1-5] the reaction is operated at high temperature, apparently more than 100 °C, and at high pressure. We have demonstrated that photocatalytic N-alkylation of amines with alcohols by suspended platinized TiO_2 particles proceeds at room temperature and ambient pressure,[6] and that both oxidation and reduction products of the TiO_2-photocatalytic reaction are efficiently utilized for the N-alkylation through the successive dark processes. This paper describes the electrolytic N-alkylation at ambient temperature as a combined process of anodic oxidation and cathodic reduction.[7]

Amines and alcohols were highest available grades (Nakarai Chemicals) and used as received. A one-chamber Pyrex cell equipped with a Pt-black-coated Pt anode, a coiled Pt cathode and an SCE reference electrode was used as a electrolysis cell. A 150 cm^3 portion of alcohol containing 0.5 mol dm^{-3} of electrolyte ($LiClO_4$ or $LiNO_3$) was placed in the cell and purged with Ar for > 30 min. Pt black (Nakarai; 50 mg) was added and purged with Ar for further 10 min. Substrate primary amine (0.5 cm^3) was injected into the cell through a rubber septum and electrolyzed either galvanostatically or potentiostatically at 25 ± 2 °C. Products were analyzed by ^1H NMR and GC and identified with authentic samples.

Table 1 shows the typical results of the electrolytic N-alkylation of benzylamine and aniline in either methanol or ethanol. These amines were chosen as typical aliphatic and aromatic amines, respectively. Ethylation of benzylamine to yield N-ethylbenzylamine proceeded selectively by both galvanostatic and potentiostatic electrolyses. The effect of water (10 vol%) was negligible in the N-ethylation. Reaction of aniline dissolved in ethanol gave N-ethylaniline together with a small amount of N-ethylideneaniline. Galvanostatic electrolysis of a $LiNO_3$ solution but not a $LiClO_4$ solution led to

Table 1. Electrolytic N-Alkylation of Amines with Alcohols

R^1NH_2 R^1 =	R^2CH_2OH R^2 =	Water vol%	Electrolyte	Electricity F mol^{-1}	Yield/%a)		Current Efficiency %
					sec-Amine	tert-Amine	
benzyl	methyl	0	$LiNO_3$	2.8 (G)b)	91	≃ 0	65
benzyl	methyl	0	$LiNO_3$	5.8 (G)d)	39	≃ 0	15
benzyl	methyl	10	$LiClO_4$	3.0 (P)c)	96	≃ 0	65
benzyl	H	0	$LiNO_3$	5.6 (G)	27	12	18
benzyl	H	10	$LiClO_4$	2.0 (P)	≃ 0	≃ 0	≃ 0
phenyl	methyl	0	$LiNO_3$	7.0 (G)	54	≃ 0	16

a)Based on the starting amine. b)Galvanostatic electrolysis at 50 mA (6.3 mA cm^{-2}). c)Potentiostatic electrolysis at +1.0 V vs SCE. d)Without Pt black.

the methylation of benzylamine to produce N-methylbenzylamine as well as the further methylated product, N,N-dimethylbenzylamine.8)

These reactions can be represented by general equations, as follows.

$$R^1NH_2 + R^2CH_2OH \longrightarrow R^1NHCH_2R^2 + H_2O \qquad (1)$$

$$R^1NH_2 + 2R^2CH_2OH \longrightarrow R^1N(CH_2R^2)_2 + 2H_2O \qquad (2)$$

Electrolyses of alcohols without amines gave aldehydes and H_2 *via* anodic oxidation of the alcohols and cathodic reduction of H^+, as Scheme 1 shows. Condensation of the aldehyde with amine proceeds feasibly to give a Schiff base intermediate,9) which would be hydrogenated into an N-alkylated product.

Figure 1 (a) shows the course of N-ethylation of benzylamine in the absence of suspended Pt black (galvanostatic; 50 mA). The main product during the electrolysis was N-ethylidenebenzylamine, which was hydrogenated into N-ethylbenzylamine predominantly when the reaction mixture was kept under the open-circuit (off current) conditions for about 24 h. Ar purge of the gaseous phase under similar open-circuit conditions markedly decreased the extent of the hydrogenation to N-ethylbenzylamine (see Fig. 1(a)). These facts suggest that the Pt-black surface of anode under open circuit catalyzes the hydrogenation of Schiff base product with cathodically liberated H_2. On the other hand, in the presence of Pt black particles the N-ethylation was enhanced considerably while much lesser increment of the conversion of Schiff base to N-ethylated product was observed under the open-circuit conditions (Fig. 1(b)). This observation indicates that the suspended Pt particles can catalyze the *in situ* hydrogenation during elctrolysis (see also Scheme 1), as was observed in the electrosynthesis of 2,5-dimethylphenyl acetate.10)

On the basis of these results the current efficiency of this electrolytic N-alkylation was evaluated as the ratio of twice of the N-alkylation product (in mol) to the passed electricity (F). The highest efficiency of > 60 % was obtained for the N-ethylation of benzylamine (see Table 1).

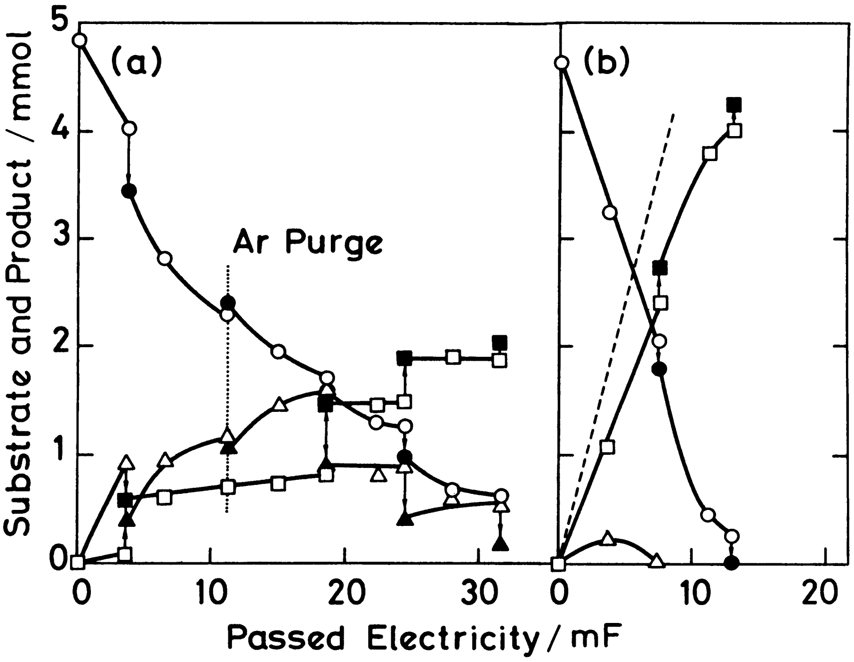
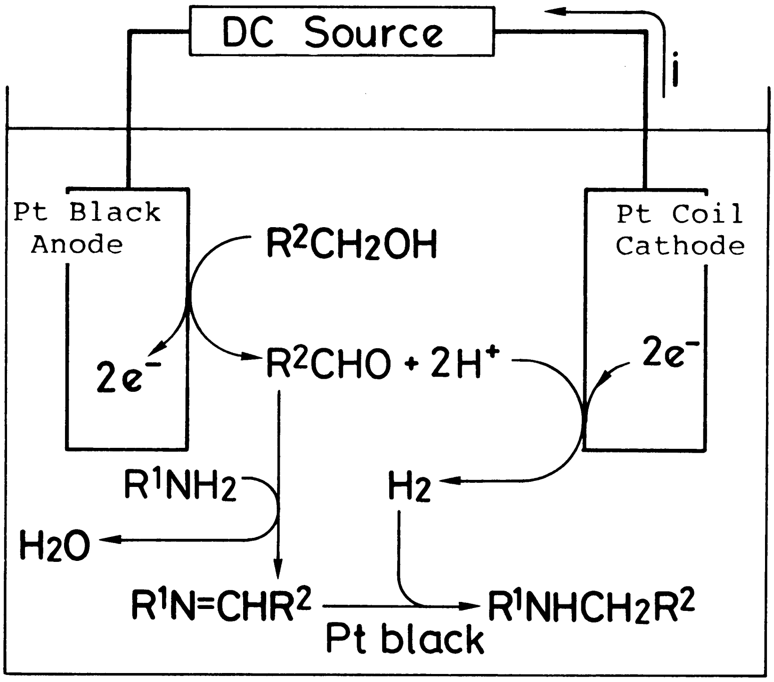


Fig. 1. Electrolytic N-ethylation of benzylamine in the (a) absence and (b) presence of Pt black suspended in ethanol; ○, ● : benzylamine, □, ■ : N-ethylbenzylamine, and △, ▲ : N-ethylidenbenzylamine. Arrows indicate the changes during the standing under open-circuit conditions for 24 h. Closed symbols represent the corresponding amounts after the standing. Dashed line shows the current efficiency of 100%. Dotted line shows Ar purge of the gaseous phase just after electrolysis.



Scheme 1. Electrolytic N-alkylation of amines with alcohols.

Thus, we have demonstrated the novel electrolytic N-alkylation process to synthesize secondary or tertiary amines from alcohols with sufficient current efficiencies.

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(Received July 30, 1986)